

Monte-Carlo Simulation of Solid-Solid Transition to Conformationally Disordered State

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ABSTRACT: CONDIS phases and transitions are of considerable importance with respect to the phase behavior of flexible chain molecules. Even low molecular weight compounds exhibit CONDIS phases where the molecules adopt highly disordered conformations as in the liquid phase but without losing long-range order (CONDIS crystal). So far the understanding of these crystals may be of interest for the description of the melting process. In this paper we present a Monte-Carlo simulation of the CONDIS phase transition based on a simple three-parameter model for particles with one internal degree of freedom. The parameters themselves can be deduced in principle from atomistic calculations. It is shown that our calculations yield a solid-liquid as well as a solid-CONDIS crystal (solid) phase transition depending on the energy difference between both states of the particle.

Introduction

In the last years there has been considerable interest in the conformationally disordered (CONDIS) crystalline state exhibited by many flexible-chain polymers and low molecular weight compounds, particularly cycloalkanes.^{1,2} Aside from a great deal of experimental work using calorimetry, NMR, vibrational spectroscopy, and other methods,³ a few attempts have been made to describe theoretically the thermodynamic behavior of the CONDIS crystals and the transition between the ordered crystal and the CONDIS crystal.³ Due to the complicated nature of the CONDIS state, however, very simplified qualitative models were tried, based on the well-known approximations of Lennard-Jones and Devonshire, Bragg and Williams, and others.³ The applicability of these models to the CONDIS state is still a point of discussion because the analogy between a system of conformationally flexible particles and the systems used in the approximate theories of Lennard-Jones and Devonshire (a lattice with holes) or Bragg and Williams (an Ising system with a statistical short-range order) is not so close. A quantitative approach of the high-pressure transition of polyethylene into the CONDIS phase was done on the basis of the cluster entropy hypothesis and with molecular parameters from semiempirical atomistic calculations.⁴

A great aid in understanding the nature of the CONDIS state can be furnished by computer experiments whose results can be compared both with the observed thermodynamic behavior of CONDIS crystals and with the results of approximate theories.

The only attempt at computer simulation of a CONDIS transition is the one recently undertaken by Sumpter et al.⁵ for the polyethylene (PE) crystal. The temperature behavior of the crystal was studied using the molecular dynamics method and an atomistic force field.⁶ The systems considered involved up to 37 mobile PE chains, and the trajectories generated were up to 30 ps. As the temperature was increased, the authors⁵ observed the appearance of conformational defects in the PE chains. However, despite a tremendous computational effort and the comparatively large size of the model system, no cooperative phenomena were observed and no changes in

the molecular packing and crystal symmetry were reported. It seems that the observation of the cooperative phenomena requires much larger systems and much longer times, which is not yet feasible even with the use of the most powerful computers and vector programming techniques.

Another problem, which can hardly be overcome using atomistic models, is the problem of "pseudo-non-ergodicity" of the configurational space.⁷ As far as the solid state is concerned in simulation of CONDIS transitions, the ordered and CONDIS states in the configurational space may well be separated by relatively high energy barriers, so that the CONDIS state is difficult to reach using molecular dynamics or Monte-Carlo chains of a finite length. Clearly, this problem should be particularly important for atomistic models because of the extremely high dimensionality of the relevant configurational space.

In view of the computational difficulties involved in simulation of the CONDIS state using atomistic force fields, a need arises for simplified semiquantitative models, which reflect only the dominant properties of the systems exhibiting the CONDIS state. In a sense, the situation with the CONDIS state is similar to the one occurring with early simulations of polymer chains on two- and three-dimensional lattices. Although the lattice models were quite artificial and could hardly be associated with specific polymers, they retained the dominant features of polymers in general and helped to gain a better insight into the conformational behavior of polymer chains.

In this work we propose a simplified model, which retains only general features inherent in systems experiencing CONDIS transitions. The starting point used to construct the model is a classical two-dimensional Lennard-Jones system, which is one of the simplest systems capable of describing the most general phenomena in the phase behavior of matter (such as melting, crystallization, and evaporation). We modify the system by introducing an intramolecular degree of freedom and the associated intramolecular (conformational) energy and by making the Lennard-Jones interaction potential conformation- and orientation-dependent. The aim of the work is to see whether these modifications are sufficient for the system to experience a CONDIS-like transition.

Model

To construct a simple generalized model for simulating the CONDIS state, let us first analyze what are the

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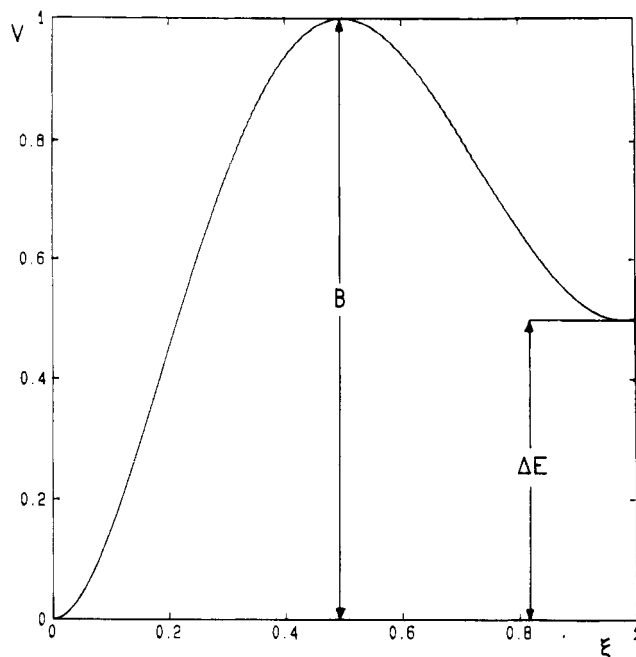


Figure 1. Typical dependence of the intramolecular energy V on the conformational parameter ξ .

dominant features necessarily present in the crystals experiencing CONDIS transitions. As any crystal, a CONDIS crystal represents a system of particles interacting via a certain intermolecular potential. The distinguishing feature of CONDIS crystals is that their constituent molecules are necessarily flexible and can assume at least two stable conformations. The flexibility means that each molecule has at least one internal degree of freedom, whose variation affects both the intramolecular energy and the form of the intermolecular interaction potential. The existence of stable conformers implies, in its turn, that the dependence of the internal energy on the internal degree of freedom must involve at least two minima separated by a barrier.

In developing our model, it is reasonable to take, as the starting point, a two-dimensional Lennard-Jones (LJ) system, which is known to be capable of simulating the most general phenomena in the phase behavior of matter (such as crystallization, melting, and evaporation). With polymers, the use of the two-dimensional representation is justified by the fact that the conformation-induced changes in the arrangement of the chains occur mostly in the planes perpendicular to the chain axes, while the phenomena occurring in the third dimension, such as chain shortening, seem to be of minor importance. The latter statement is supported by the fact that CONDIS transitions may well occur in low molecular weight crystals, in which the effect of the chain shortening is absent.

To adapt the LJ system to our particular case, let us assume that each particle i in the system has an internal or "conformational" degree of freedom, ξ_i , which varies in the range from 0 to 1. Let us also ascribe a "conformational energy" $V(\xi_i)$ to each particle i . The particular dependence used in this work for $V(\xi_i)$ is shown in Figure 1. This is a fifth-order dependence

$$V = A_5\xi^5 + A_4\xi^4 + A_3\xi^3 + A_2\xi^2 \quad (1)$$

with minima at $\xi = 0$ and 1 and a maximum at $\xi = 0.5$. The coefficients of the polynomial are chosen so that the energy difference ΔE and the barrier B are equal to some prescribed values. (Two more conditions needed to specify the four unknown coefficients A_i in eq 1 are given by the

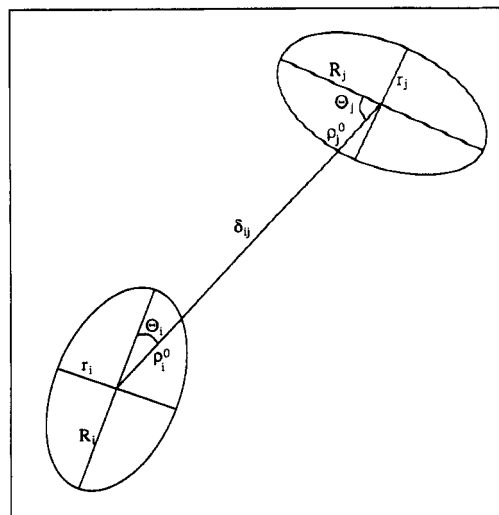


Figure 2. Definition of the geometrical parameters of the interaction potential φ .

constraints $dV/d\xi = 0$ at $\xi = 0.5$ and 1 .) So, ΔE and B are the two first parameters of the model.

The next step is to make the shape of the initially symmetrical LJ potential

$$\varphi_{ij} = \epsilon_{ij}[(\delta_{ij}/\delta_{ij}^0)^{-12} - 2(\delta_{ij}/\delta_{ij}^0)^{-6}] \quad (2)$$

dependent on the mutual orientation and conformations of the interacting molecules. This can be accomplished by incorporating an orientational and conformational dependence in the equilibrium distance δ_{ij}^0 and depth ϵ_{ij} of the potential. For the equilibrium distance, this is done by writing δ_{ij}^0 in the usual form of the geometrical mean³

$$\delta_{ij}^0 = [(2\rho_i^0)(2\rho_j^0)]^{1/2} \quad (3)$$

and then assuming that the equilibrium molecular radii, ρ_i^0 and ρ_j^0 , depend on the conformation and mutual orientation of the interacting molecules.

The angular dependence for ρ^0 is chosen such that $\rho^0(\theta)$ forms an ellipsis around the molecular center (see Figure 2 for the definition of θ). The shape of the ellipsis depends on the relevant conformational parameter ξ in such a way that at $\xi = 0$ the ellipsis degenerates to a circle, and then, with increasing ξ , the ellipsis becomes more and more extended until it reaches a certain limiting allowable ellipticity characterized by a constant $\gamma_1 < 1$. As a measure of ellipticity, it is convenient to use parameter γ which varies from 1 to γ_1 and defines the short and long radii of the ellipsis, r and R (see Figure 2), by the relations

$$r = R_0\gamma \quad R = R_0/\gamma \quad \gamma = (r/R)^{1/2} \quad (4)$$

where R_0 is a constant.

The explicit relation between γ and ξ may then be set to be

$$\gamma = 1 - (1 - \gamma_1)\xi \quad (5)$$

that is, at $\xi = 0$, $\gamma = 1$, and $r = R = R_0$, the ellipsis degenerates to a circle of radius R_0 ; at $\xi = 1$, $\gamma = \gamma_1 = (r/R)^{1/2}$, the ellipsis has the greatest allowed extension. It is noteworthy that with the above definitions, any variation in ξ leaves the ellipsis' area unchanged

$$\pi Rr = \pi R_0^2 \quad (6)$$

and equal to the area of a circle of radius R_0 (hereinafter, the "equivalent circle").

With the above definitions, the analytical expression for ρ^0 can be readily shown to be

$$(\rho^0)^2 = R_o^2 \gamma^2 / [\cos^2 \theta (\gamma^4 - 1) + 1] \quad (7)$$

so that

$$\begin{aligned} (\delta_{ij}^0)^2 &= \frac{4R_o^2 \gamma_i \gamma_j}{[\cos^2 \theta_i (\gamma_i^4 - 1) + 1]^{1/2} [\cos^2 \theta_j (\gamma_j^4 - 1) + 1]^{1/2}} \\ &= D_o^2 \alpha \end{aligned} \quad (8)$$

where α contains all the angular and conformational dependence and $D_o = 2R_o$, the diameter of the equivalent circle or the equilibrium separation between the centers of two such circles. It is reasonable to take D_o as the unit of distance and to measure all distances in the model system in terms of D_o .

For the potential depth ϵ_{ij} , the angular and conformational dependence is reasonable to take in the form

$$\epsilon_{ij} = \epsilon_o R_o^2 / \rho_i^0 \rho_j^0 = \epsilon / \alpha \quad (9)$$

that is, if one approaches the ellipsis on its wide side, the potential minimum is deep, and it is shallow in the case of the narrow side. This reflects the fact that the interaction potential of two organic molecules is roughly proportional to the size of each molecule in the direction of interaction.⁶ With the above choice, $\epsilon_{ij} = \epsilon_o$ if both interacting molecules are in the circular conformation. If they are ellipses with the largest allowable ellipticity, then $\epsilon_{ij} = \epsilon_o \gamma_i^2$ for the linear configuration (the weakest interaction), $\epsilon_{ij} = \epsilon_o / \gamma_i^2$ for the parallel configuration (the strongest interaction), and $\epsilon_{ij} = \epsilon_o$ for the perpendicular (T-shaped) configuration. As with D_o , it is reasonable to take ϵ_o as the unit of energy.

Substituting (8) and (9) into (2) and assuming $D_o = \epsilon_o = 1$, we obtain the final form of the interaction potential

$$\varphi_{ij} = \alpha^5 \delta_{ij}^{-12} - 2\alpha^2 \delta_{ij}^{-6} \quad (10)$$

To summarize, the generalized model suggested in this section represents a classical two-dimensional system of LJ particles, each possessing one internal or conformational degree of freedom ξ ranging from 0 to 1. Associated with this degree of freedom is an internal or conformational energy $V(\xi)$ characterized by two minima at the two limiting values of ξ . The intermolecular interaction potential gradually changes its symmetry from circular to elliptical on variation of ξ from 0 to 1. Altogether, the model involves three parameters: ΔE , the energy difference between the circular and elliptical conformers; B , the barrier separating the internal energy minima; and γ_1 , the square root of the lowest allowable ratio of the short and long ellipses' radii. The latter parameter, γ_1 , characterizes the extent of the geometrical changes occurring on going from one conformer to the other. Whereas ΔE and B have a clear physical meaning and can be related, in a more or less straightforward way, to the properties of a real molecule, this is not so easy with γ_1 . Nevertheless, for the purposes of a qualitative analysis the parameter γ_1 appears to be quite suitable. It would be hardly reasonable to require more from a simplified model.

Monte-Carlo Procedure

The technique used was a standard NVT-ensemble technique⁷ involving periodic boundary conditions and a cyclic procedure for molecular displacements. For the number of particles in the periodic box, N , several discrete values were tried between 36 and 336. Most calculations were conducted with $N = 36$. In the high- and mid-density regions, the effect of increasing the number

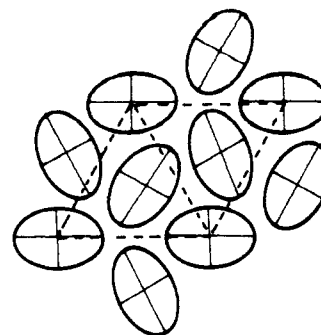


Figure 3. Fragment of the structure corresponding to the minimum energy packing of ellipses with $\xi = 1$.

of particles was negligible: an $N = 36$ system showed practically the same structure and thermodynamic properties as a system containing as many as 336 particles. The size of the system became, however, important in the solid-liquid transition region. Here small systems tended to exaggerate the stability of the solid state because of an extra periodicity imposed upon the system by the periodic boundary conditions.

A typical MC chain involved 3×10^6 cycles, that is $N(3 \times 10^6) = 10^7$ to 10^8 random configurations. The first 1×10^6 cycles were only used to bring the system to a more or less equilibrium state and were not included in the averaging.

The structure and phase state of the system were analyzed using the following distribution functions: $r(\delta)$, the radial distribution function, i.e., the probability of finding a molecule at a distance δ from another molecule; $a(z)$, the angular distribution of a molecule's nearest neighbors (To calculate $a(z)$ during the MC run, an arbitrary molecule was selected and its six closest neighbors were found. Then the molecule at the center was joined by straight lines with its neighbors to give six virtual bonds. One arbitrary bond was taken as a reference one and the angles z between this bond and the other five were calculated and averaged over the chain); $c(\theta)$, the angular correlation function characterizing the distribution of mutual orientations of neighboring molecules (To calculate $c(\theta)$, an arbitrary molecule and its six neighbors were selected. Then the angles formed by the long molecular axes of the center molecule and the neighboring ones were calculated and averaged over the chain. Each contribution from molecules i and j was given a weight $\xi_i \xi_j$, so that the contribution was the greater, the more elliptical the molecules); $o(z)$, the orientational distribution of molecules, defined as the probability density of finding a molecule whose long axis forms an angle z with the x -axis of the periodic box (When $o(z)$ was calculated, each contribution from molecule i was given a weight ξ_i); $p(\xi)$, the distribution of molecules over conformations, i.e., the probability density of finding a molecule with a conformational parameter equal to ξ .

Considering the problem of non-ergodicity,⁷ which might well arise as far as the solid state was concerned, much attention was given to check if the equilibrium structure and thermodynamic quantities resulting from MC calculations depend on the starting configuration used to initiate the random walk. In doubtful cases, in which the appearance of metastable states could be expected, the results were recalculated using different starting configurations. The set of starting configurations used included a hexagonal close packing of circles with a random orientation of the molecular axes and three distinct regular packings of ellipses with $\xi = 1$. Also used as a starting configuration was a packing of ellipses ($\xi = 1$) corresponding to the minimum static potential energy. It is essential that the lattice of the molecular centers in the lowest energy structure does not have an exact hexagonal symmetry. Such a symmetry would only occur if the centers of the molecules inside the unit cell would coincide with the centers of the respective triangles in Figure 3. In the actual fact, the molecular centers are markedly shifted from the centers of the triangles. As a result, a 60° rotation of the whole structure around the origin of the unit cell does not superimpose the new positions of the molecular centers onto their previous positions.

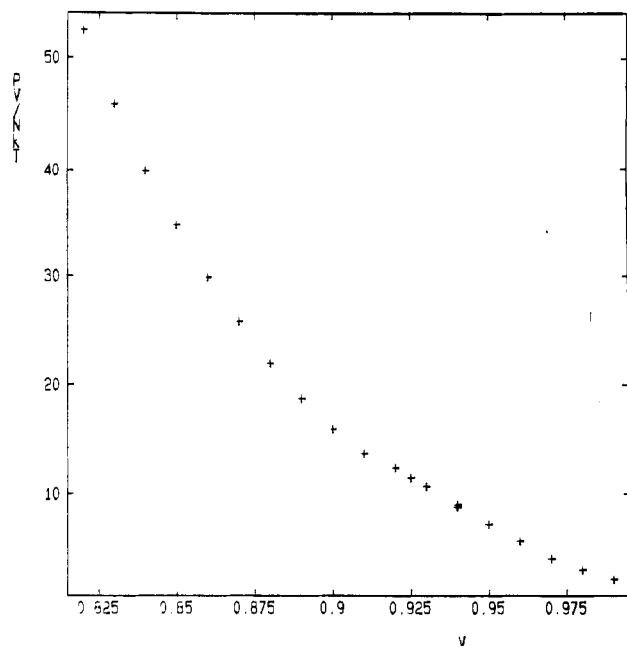


Figure 4. Solid-liquid transition: $P(V)$ isotherm for $\Delta E = -0.5$.

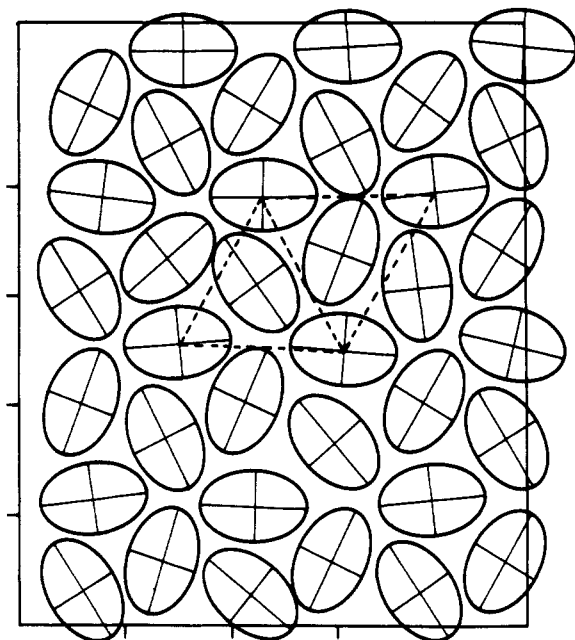


Figure 5. Structure of the high-pressure phase at $V = 0.84$ for $N = 36$, $\Delta E = -0.5$.

Results and Discussion

In this paper we present our Monte-Carlo results for $kT = 0.25$ and the following set of model parameters: $\gamma_1 = 0.8$, $\Delta E = \pm 0.5$, $B = 1$. We start the discussion with the results for $\Delta E = -0.5$ (ellipses with $\gamma = \gamma_1$ are more stable than circles). The respective $P(V)$ isotherm shown in Figure 4 consists of two branches. The high-pressure branch, which extends up to $V = 0.9$, corresponds to an ordered solid phase. The thermodynamic properties and structure of this phase were practically independent on the starting configuration used to initiate the Monte-Carlo run. So, we dealt with a stable state of our model system.

A typical crystal structure of the high-pressure phase and the relevant distribution functions are presented in Figures 5 and 6. By comparing Figures 3 and 5, one can conclude that the high-pressure structure essentially coincides with the minimum static energy structure, except for slight thermal perturbations. A characteristic feature

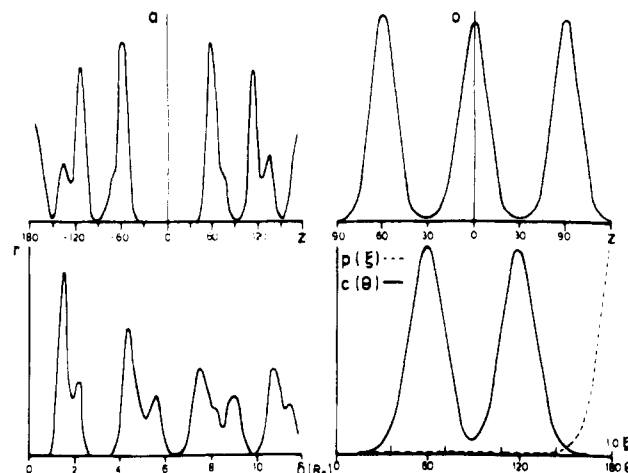


Figure 6. Distribution functions of the high-pressure phase at $V = 0.84$ for $N = 36$, $\Delta E = -0.5$.

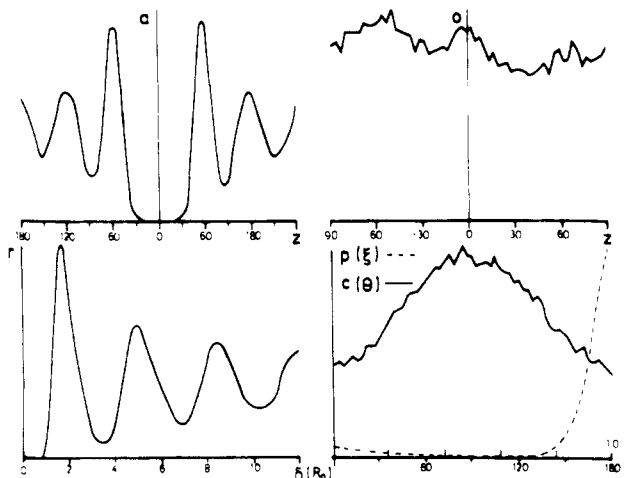


Figure 7. Distribution functions for the low-pressure (liquid) phase at $V = 0.98$ for $N = 36$, $\Delta E = -0.5$.

of this structure is the presence of a small satellite in the first peak of $r(\delta)$, due to the occurrence of symmetrically distinct molecules in the unit cell. Similar satellites are also observed in $a(z)$. Most of the particles in the high-pressure phase are elliptical (see the distribution $p(\xi)$ in Figure 6). The average value of the conformational parameter, $\langle \xi \rangle$, is about 0.95.

The low-pressure branch of the $P(V)$ isotherm ($V > 0.95$) refers to a liquid phase, which is well seen from the distribution functions shown in Figure 7. Most of the particles remain elliptical ($\langle \xi \rangle = 0.88$ at $V = 1.0$).

The mid-pressure range between $V = 0.91$ and 0.95 represents a so-called "interval of confusion".⁷ The resulting phase state of the system was here strongly dependent on what particular starting configuration was used in the Monte-Carlo run: some configurations resulted in a liquid phase, while the others in a solid phase. The occurrence of such a confusion interval is quite typical of the regions of phase transition.⁷ To summarize, for $\Delta E = -0.5$ the system of conformationally flexible particles exhibited a usual solid-liquid transition.

Now we turn to the case of $\Delta E = +0.5$ (ellipses are less stable than circles). The isotherm presented in Figure 8^{8,9} looks similar to the one for $\Delta E = -0.5$. At high pressures, again, an ordered solid phase results, whose structure and distribution functions are nearly identical to those discussed above. Up to $V = 0.85$ most of the particles remain elliptical, $\langle \xi \rangle = 0.9$, despite the fact that the intramolecular energy favors the circles. This is not surprising because the stability of a particular structure is governed by the

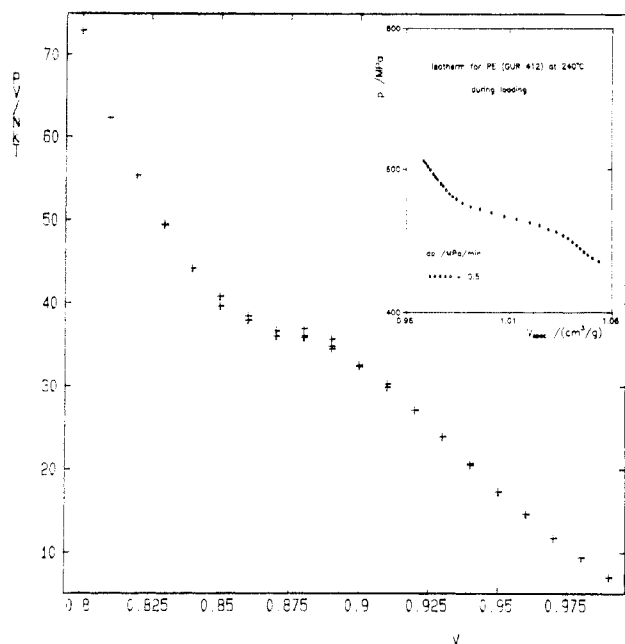


Figure 8. Ordered solid-CONDIS solid transition: $P(V)$ isotherm for $\Delta E = 0.5$.

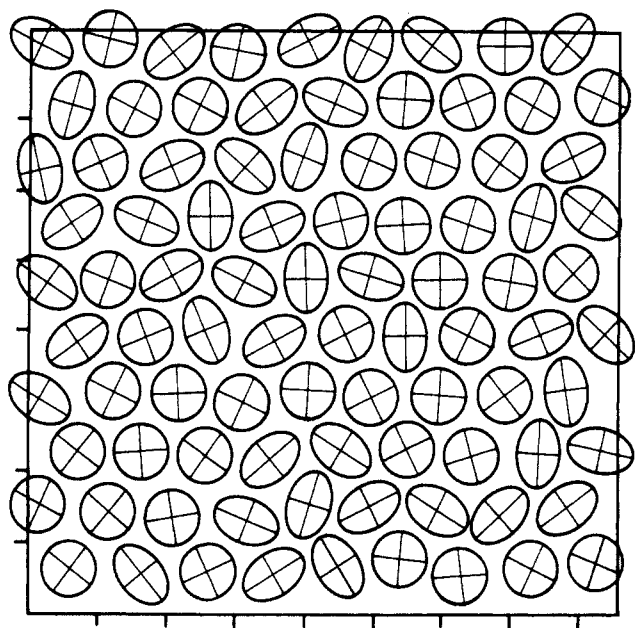


Figure 9. Typical structure of the low-pressure CONDIS phase at $V = 0.92$ for $N = 90$, $\Delta E = 0.5$.

total free energy and not by the intramolecular energy alone. For the particular interaction potential used, the obvious contribution, which favors the ellipses, is the packing energy, which strongly prefers the ellipses, particularly at high pressures.

At $0.85 < V < 0.90$ one again observes an interval of confusion where the resulting structure of the Monte-Carlo run is dependent on the starting configuration. Unlike the case of $\Delta E = -0.5$, however, drastic conformational changes occur in this interval: the average conformational parameter $\langle \xi \rangle$ falls from 0.9 to 0.5, that is nearly a half of the molecules convert to circles.

At $V > 0.9$ a new stable branch in the $P(V)$ isotherm appears. A typical structure and distribution functions observed in this range are presented in Figures 9 and 10. As follows from the presence of zero-density gaps in $r(\delta)$ and $a(z)$, the system remains solid. Moreover, even some orientational order of ellipses still exists, as seen from the occurrence of three well-defined peaks in $o(z)$. At the

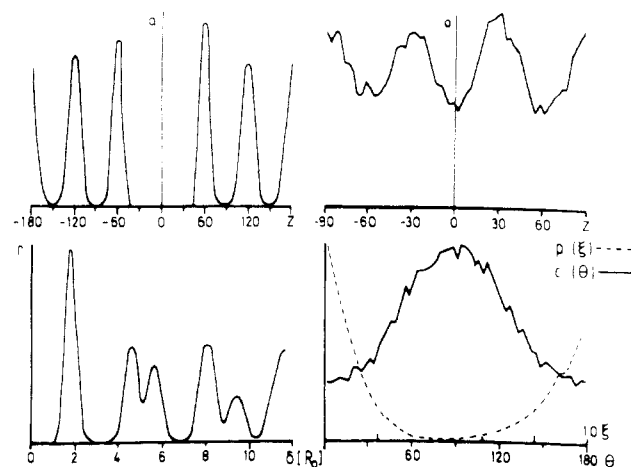


Figure 10. Distribution functions of the low-pressure phase at $V = 0.92$ for $N = 90$, $\Delta E = 0.5$.

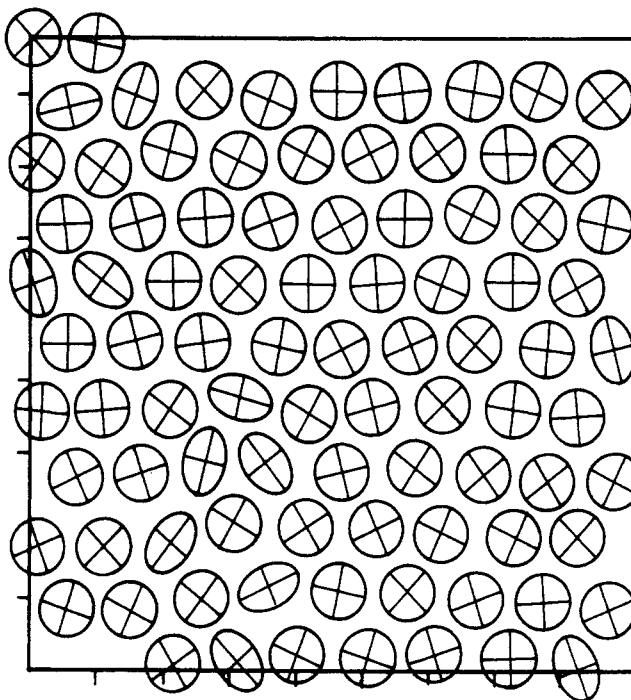


Figure 11. Similar conformers showing a slight trend of clustering at high volumes $V = 1.03$ for $N = 90$, $\Delta E = 0.5$.

same time, the characteristic satellites in $r(\delta)$ and $a(z)$ disappear and the average structure assumes an exact hexagonal symmetry. The system represents a mixture of circles and ellipses (see the distribution $p(\xi)$ in Figure 10), with the average conformational parameter $\langle \xi \rangle$ gradually changing from 0.5 at $V = 0.9$ to 0.2 at $V = 1.02$. The transition from the high-pressure branch to the low-pressure one is accompanied by an appreciable increase in volume.

Thus the behavior of our model system reproduces all essential features typical of CONDIS transitions: the transition results from the appearance of conformationally distinct particles in the system, it is accompanied by a rise in crystal symmetry, as well as an increase in volume.

It is noteworthy that in a CONDIS system with $N > 90$ a slight trend to clustering of similar conformers was observed, so that the ellipses tended to be together (see Figure 11). Such a clustering has been previously predicted by Wunderlich³ based on a simple Lennard-Jones and Devonshire treatment. With a 36-particle system the clustering could not occur because of the small size of the system.

Conclusions

The above discussed results show that the simple three-parameter model suggested in section 2 of this work is adequate enough to reproduce most essential features of the CONDIS state and ordered crystal-CONDIS crystal transitions. The next step will be to explore the range of the model parameters, temperatures, and pressures to reveal the regions of stability of the CONDIS state. It appears that the model will be capable of describing not only the CONDIS state but also the plastic and liquid-crystal states, so that it will be possible to simulate, within a single model, all types of the disordered solid state. Also, the suggested model seems to be useful in molecular dynamics simulations to investigate the dynamic properties of the CONDIS state.

The generalized model suggested in this paper has an obvious advantage over structure-related models describing particular polymers. Indeed, our model enables continuous variation of its parameters and thus enables one to reveal what changes in conformation (γ_1) or energy (ΔE) are required for the CONDIS phase to occur. Eventually, this opportunity allows one to gain a deeper insight into the nature of the CONDIS transitions and to

understand why some particular crystals exhibit CONDIS transitions while the others do not.

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